



## Oxygen storage capacity of $\text{CuMO}_2$ ( $M = \text{Al, Fe, Mn, Ga}$ ) with a delafossite-type structure

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### ABSTRACT

Delafossite-type  $\text{CuMO}_2$  ( $M$ : trivalent cation) compounds were synthesized and found to exhibit oxygen storage capacity under oxidation/reduction cycle. The oxygen storage capacity values of  $\text{CuFeO}_2$  and  $\text{CuMnO}_2$  at lower temperature were larger than those of  $\text{CuAlO}_2$ ,  $\text{CuGaO}_2$ - and  $\text{CeO}_2$ -based materials. The large OSC includes an oxygen uptake at low temperature attributed to formation of metallic Cu by decomposition of the delafossite phase for  $\text{CuFeO}_2$  and  $\text{CuMnO}_2$ . In the case of  $\text{CuAlO}_2$ , which remained without decomposition below 800 °C, the oxygen uptake increased with temperature up to 0.13 mol-O/mol- $\text{CuMO}_2$ . The stability of the delafossite-type  $\text{CuMO}_2$  against oxidation/reduction cycle is affected by  $M^{3+}$ . In this study, it was found that the oxygen storage behavior of  $\text{CuMO}_2$  can be controlled by a combination of Cu and M ions.

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### 1. Introduction

Pollutants in automobile exhaust gas, including carbon monoxide (CO), nitrogen oxides ( $\text{NO}_x$ ) and hydrocarbons (HC), are removed by a three-way catalyst (TWC) composed of precious metal catalyst and promoters supported on  $\text{Al}_2\text{O}_3$ . TWC performance is affected by compositional fluctuation of the exhaust gas. In the pollutant removal process, CO and HC are oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , and  $\text{NO}_x$  is reduced to  $\text{N}_2$ . Therefore, the conversions of CO and HC decrease in reductive atmosphere, while conversion of  $\text{NO}_x$  decreases in oxidative atmosphere.

In order to enhance TWC performance by suppression of the cyclic oxidative (lean)–reductive (rich) compositional fluctuation in exhaust gas, metal oxides whose oxidation state can change easily have been used. At present,  $\text{CeO}_2$ -based solid solutions are widely used as promoters having oxygen storage capacity (OSC) [1,2].  $\text{CeO}_2$  exhibits oxygen storage/release behavior in oxidative/reductive atmosphere, which is accompanied by the redox of Ce ions between the oxidation states of  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$ .  $\text{CeO}_2$ – $\text{Al}_2\text{O}_3$  composite and perovskite-type oxides were also reported as new-type OSC materials [3,4]. Although it was found that copper/copper oxide system had oxygen storage/release ability in an automobile exhaust system, it caused fragmentation due to large volume change [5]. As non-stoichiometric fluorite-type  $\text{CeO}_{2-x}$  phase can

stably form in reductive atmosphere, the volume change of  $\text{CeO}_{2-x}$  accompanying the redox of  $\text{Ce}^{3+}/\text{Ce}^{4+}$  is smaller than that in the case of a metal/metal oxide such as Cu/CuO. Therefore,  $\text{CeO}_2$  is stable enough during oxygen storage/release process for use in an actual exhaust gas. Improvement of catalytic performance, especially of catalytic activity at low temperature and under oxygen-rich condition, has become necessary for compliance with recent automobile emission regulations. In order to improve activity at low temperature, it would be effective to use a promoter which exhibits a large OSC in the low temperature range. Therefore, Cu-containing oxides are suitable as promoters because they enable the reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  to occur in a lower temperature range than that of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ . As pointed out above, oxidation and reduction reactions between copper and a copper oxide involve a large volume change that leads to fragmentation of the catalyst. Therefore, a metal oxide without large structural transformation during oxidation/reduction cycle would be suitable as the TWC promoter.

In order to develop a material exhibiting oxygen storage/release behavior at lower temperature, we focused on Cu-containing delafossite-type oxides expressed by the general formula  $\text{CuMO}_2$  ( $M$  = trivalent cation) for use as OSC materials. Fig. 1 shows the crystal structure of 3R-type delafossite,  $\text{CuFeO}_2$ .  $\text{CuMO}_2$  has a layered structure consisting of edge-shared  $\text{MO}_6$  octahedra and two-coordinated  $\text{Cu}^+$  cations at the interlayer sites. There have been reported non-stoichiometric delafossite-type oxides such as  $\text{CuLaO}_{2+x}$ ,  $\text{CuYO}_{2+x}$  and  $\text{CuFeO}_{2+x}$  which have extra oxide ions at the interlayer between  $\text{MO}_6$  octahedra sheets [6,7]. This intercalation

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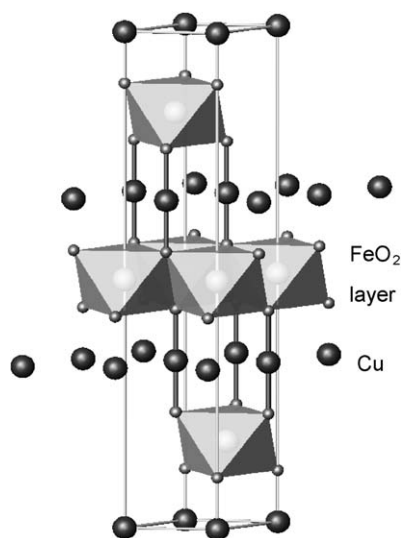


Fig. 1. Crystal structure of 3R-type  $\text{CuFeO}_2$ .

of oxide ions accompanies oxidation of  $\text{Cu}^+$  to  $\text{Cu}^{2+}$ . Although change in oxygen storage and release behavior with temperature in air has been reported for  $\text{CuLnO}_2$  (Ln: La, Y, Pr, Nd, Sm, Eu, Sc) [8–10], the behavior in cyclic oxidative–reductive atmosphere has not been investigated.

In this work, we synthesized delafossite-type copper oxides,  $\text{CuMO}_2$  ( $M = \text{Al, Mn, Fe, Ga}$ ), and investigated their OSC under cyclic oxidative–reductive atmosphere using a pulse injection method. Phase stability of the delafossite oxides against both oxidative and reductive atmospheres was also investigated in order to find a candidate material for a TWC promoter.

## 2. Experimental

$\text{CuMO}_2$  ( $M = \text{Al, Fe, Ga, Mn}$ ) compounds were synthesized by a conventional solid state reaction.  $\text{Cu}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$ , and  $\text{MnCO}_3$  were used as starting materials. The stoichiometric mixtures were obtained by ball milling using ethanol and pressed into pellets of 10 mm diameter. The pellets were heated at 860–1150 °C for 6–36 h in  $\text{N}_2$  flowing at 200  $\text{cm}^3/\text{min}$ . In order to enhance the synthetic reaction, grinding, reforming and firing processes were repeated several times. Phase identification of the oxides was performed by a powder X-ray diffraction (XRD) method using Ni-filtered  $\text{Cu K}\alpha$  radiation (RIGAKU RAD-C and MiniFlex diffractometer). Weight change of samples was measured by thermogravimetry (TG-DTA, RIGAKU TG8120, heating rate 10 °C/min) and specific surface areas of samples were estimated by  $\text{N}_2$  adsorption method (Nippon BEL, Belsorp Mini II).

The OSC of each oxide was estimated by the pulse injection method according to Yao and Yu Yao [1], using  $\text{H}_2$  gas instead of CO. This OSC value was used as an index of reversible oxygen uptake in the oxidation/reduction cycle. The oxide sample (25–50 mg) was placed in a quartz reactor and heated in He flow (200  $\text{cm}^3/\text{min}$ ) at 800 °C for 15 min prior to pulse injection. Then, it was completely oxidized by injecting 50%  $\text{O}_2/\text{He}$  pulses until a 100% breakthrough was attained.  $\text{H}_2$  and 50%  $\text{O}_2/\text{He}$  pulses were alternately injected into the oxide with He gas flowing at 200  $\text{cm}^3/\text{min}$  until constant  $\text{O}_2$  uptake was found. The volume of a pulse was 1.16  $\text{cm}^3$ . The amounts of  $\text{O}_2$  and  $\text{H}_2$  in the effluent gas were monitored with a gas chromatograph (Shimadzu GC8A) equipped with a TCD detector. OSC of the oxide was estimated from the amount of  $\text{O}_2$  uptake at 200–800 °C. The dynamic reduction behavior was evaluated by temperature-programmed reduction (TPR), which was performed

using a fixed bed flow system. The oxide sample (~50 mg) was placed in a quartz reactor and heated at 10 °C/min in a stream of 3%  $\text{H}_2/\text{He}$  (100  $\text{cm}^3/\text{min}$ ) in the temperature range 100–800 °C. The amount of  $\text{H}_2$  in the effluent gas through the oxide was monitored with a TCD detector. A liquid  $\text{N}_2$ -trap was attached in a gas line between the reactor and the detector to remove  $\text{H}_2\text{O}$  in the effluent gas.

## 3. Results and discussion

### 3.1. Synthesis and OSC of $\text{CuMO}_2$ ( $M = \text{Al, Fe, Ga, Mn}$ )

Fig. 2 shows XRD patterns for  $\text{CuMO}_2$  ( $M = \text{Al, Fe, Ga, Mn}$ ) compounds, which were synthesized under the conditions set out in Table 1. The formation of 3R-delafossite-type oxides was confirmed from the XRD patterns for  $\text{CuAlO}_2$ ,  $\text{CuFeO}_2$  and  $\text{CuGaO}_2$  by comparison with ICDD-PDF files 39-0246, 35-1401 and 41-0255 for  $\text{CuFeO}_2$ ,  $\text{CuAlO}_2$  and  $\text{CuGaO}_2$ , respectively. For  $\text{CuMnO}_2$ , the diffraction peaks were indexed on the basis of a monoclinic unit cell. This result corresponds to a delafossite-type structure with a distortion of  $\text{MnO}_6$  octahedra due to the Jahn-Teller effect of  $\text{Mn}^{3+}$  [11].

The oxygen storage capacities of  $\text{CuMO}_2$  estimated as a function of temperature by the pulse injection are shown in Fig. 3. Specific surface areas of  $\text{CuMO}_2$  were listed in Table 1. Oxygen storage behavior was observed at 300 °C for  $\text{CuFeO}_2$  and  $\text{CuMnO}_2$ . OSC of  $\text{CuFeO}_2$  and  $\text{CuMnO}_2$  was 120 and 265  $\mu\text{mol-O}_2/\text{g}$  at 300 °C, respectively, and increased with temperature to 500 °C. In the temperature range from 500 to 700 °C,  $\text{CuFeO}_2$  and  $\text{CuMnO}_2$  showed higher OSC of over 700  $\mu\text{mol-O}_2/\text{g}$ . However, decrease of OSC was observed for  $\text{CuFeO}_2$  above 700 °C. The OSC of  $\text{CuGaO}_2$  and  $\text{CuAlO}_2$  was less than 100  $\mu\text{mol-O}_2/\text{g}$  below 500 °C and increased steeply at 600 °C for  $\text{CuGaO}_2$  and at 800 °C for  $\text{CuAlO}_2$ . In the case of

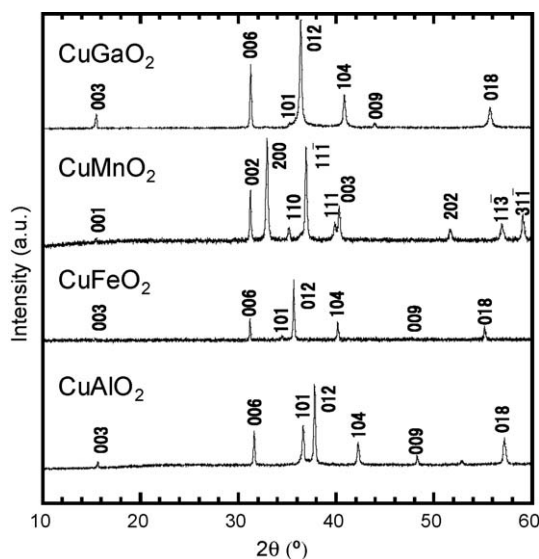


Fig. 2. XRD patterns for  $\text{CuMO}_2$  ( $M = \text{Al, Fe, Ga, Mn}$ ).

Table 1

Synthesis conditions and specific surface area ( $S$ ) of  $\text{CuMO}_2$  ( $M = \text{Al, Fe, Mn, Ga}$ ).

M	Temperature (°C)	Heating time, h	Structure of product	$S$ ( $\text{m}^2/\text{g}$ )
Fe	1100	6	3R-delafossite	1
Al	1150	24	3R-delafossite	1
Mn	960	36	Monoclinic	2
Ga	860	24	3R-delafossit	1

All the samples were heated in  $\text{N}_2$  flow at 200  $\text{cm}^3/\text{min}$ .

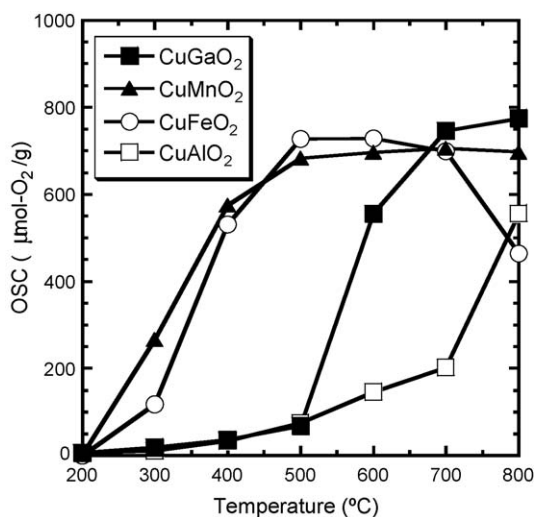


Fig. 3. OSC of  $\text{CuMO}_2$  as a function of temperature.

$\text{CuGaO}_2$ , the OSC reached  $775 \mu\text{mol-O}_2/\text{g}$  at  $800^\circ\text{C}$ , which is compared to the maximum value for  $\text{CuFeO}_2$  and  $\text{CuMnO}_2$ . Fig. 4 shows XRD patterns of  $\text{CuMO}_2$  samples after OSC measurement up to  $800^\circ\text{C}$ . Partial decomposition of the delafossite phase was observed for  $\text{CuFeO}_2$ ,  $\text{CuMnO}_2$  and  $\text{CuGaO}_2$ . The peaks of metallic Cu were observed for those oxides, indicating reductive decomposition occurred. Moreover,  $\text{Fe}_3\text{O}_4$  and  $\text{Mn}_3\text{O}_4$  formed after decomposition of  $\text{CuFeO}_2$  and  $\text{CuMnO}_2$ , respectively. The presence of Fe and Mn oxides including their divalent ions indicates that  $\text{Fe}^{3+}$  and  $\text{Mn}^{3+}$  in the delafossite-type oxides also reduced during the measurement. In the case of  $\text{CuAlO}_2$ , the delafossite phase remained as a single phase after the measurement. These results suggest that the stability of  $\text{CuMO}_2$  delafossite-type oxide is affected by  $\text{M}^{3+}$  ions, which occupy the octahedral sites. As  $\text{Fe}^{3+}$  and  $\text{Mn}^{3+}$  are more easily reduced to divalent ions than  $\text{Al}^{3+}$  and  $\text{Ga}^{3+}$ , decomposition of  $\text{CuFeO}_2$  and  $\text{CuMnO}_2$  would be caused by structural change of edge-shared  $\text{MO}_6$  octahedra layer in reductive atmosphere.

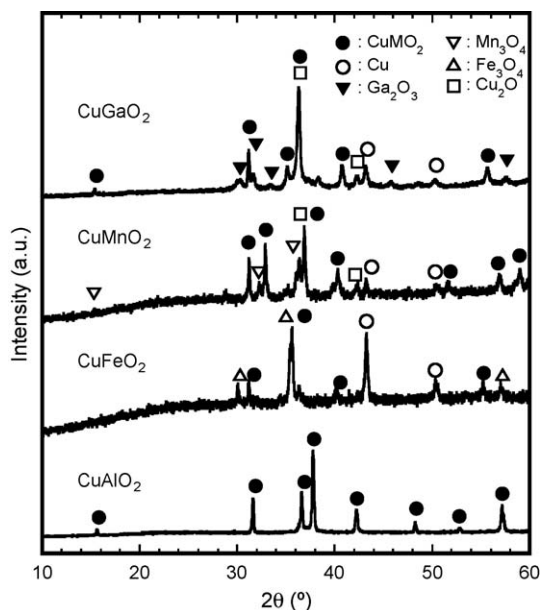


Fig. 4. XRD patterns of  $\text{CuMO}_2$  samples after OSC measurement.

### 3.2. Oxidation and reduction behavior of $\text{CuMO}_2$

In order to investigate oxidation and reduction behavior of the delafossite phase during measurement of OSC, oxidized and reduced  $\text{CuFeO}_2$  and  $\text{CuMnO}_2$  samples were prepared by injection of  $\text{O}_2$  or  $\text{H}_2$  pulse at  $300$ – $600^\circ\text{C}$ . 25 or 50 mg of samples were used in order to change a  $W/F$  at the treatments, which were 0.0075 and  $0.015 \text{ g s}/\text{cm}^3$ , respectively. Prior to these treatments, the samples were heated in He flow at  $800^\circ\text{C}$  for 15 min. Fig. 5 shows XRD patterns of oxidized and reduced  $\text{CuFeO}_2$ . The delafossite-type  $\text{CuFeO}_2$  remained as a single phase for the oxidized samples at  $400$ – $600^\circ\text{C}$ , while formation of Cu was observed for the reduced samples. Fig. 6 shows XRD patterns of reduced  $\text{CuFeO}_2$  samples with a different  $W/F$  at  $300^\circ\text{C}$ . The formation of Cu was also observed even at short contact time ( $W/F = 0.015$ ). From a result of TPR measurement, reduction peak of these oxides observed below  $350$  and at  $350$ – $500^\circ\text{C}$ , for  $\text{Cu}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$ , respectively, however, reduction of Cu oxide occurred without reduction of  $\text{Fe}^{3+}$  during the treatment. XRD patterns of oxidized and reduced  $\text{CuMnO}_2$  are

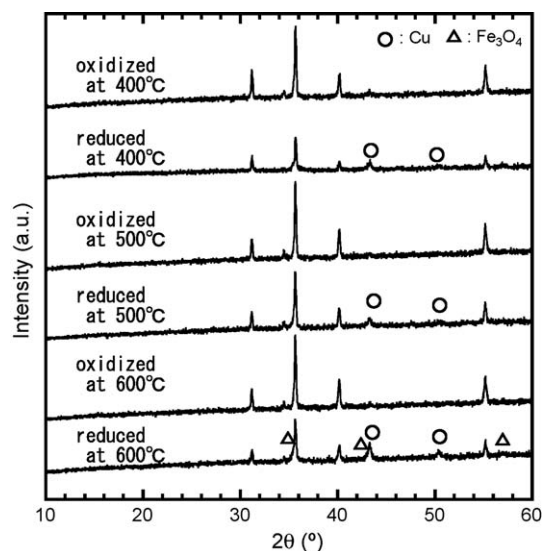


Fig. 5. XRD patterns of  $\text{CuFeO}_2$  after oxidizing and reducing treatments ( $W/F = 0.0075 \text{ g s}/\text{cm}^3$ ).

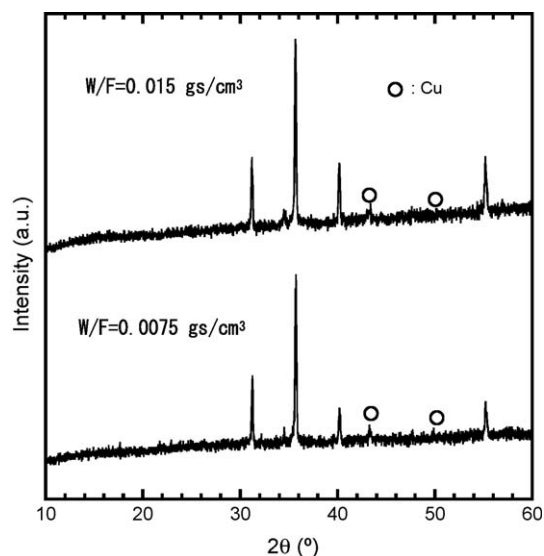


Fig. 6. XRD patterns of  $\text{CuFeO}_2$  after reducing treatment at  $350^\circ\text{C}$ .

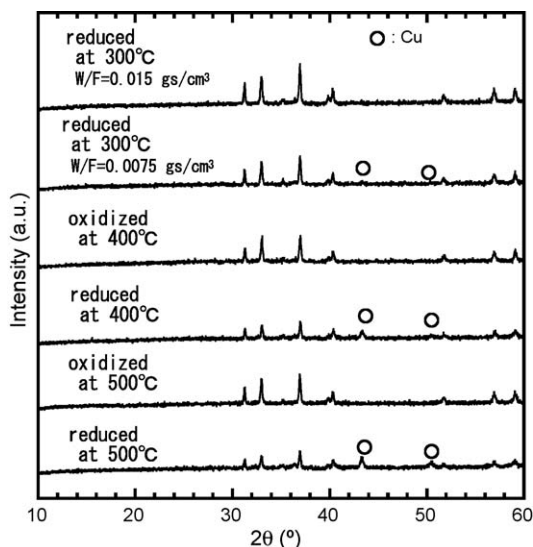


Fig. 7. XRD patterns of  $\text{CuMnO}_2$  after oxidizing and reducing treatments.

shown in Fig. 7. In the case of oxidized samples, delafossite-type phases remained without Cu formation. For the reduced samples at 300–500 °C, Cu formation was observed and in the case of larger W/F at 300 °C, no metallic Cu formed even in reductive condition. Table 2 shows OSC values of  $\text{CuFeO}_2$  and  $\text{CuMnO}_2$  in different W/F conditions at 350 and 300 °C, respectively. The OSC values for  $\text{CuFeO}_2$  were close to each other and smaller OSC was observed in the case of short contact time ( $W/F = 0.015$ ) for  $\text{CuMnO}_2$ . These results suggest that non-stoichiometric delafossite phase of  $\text{CuMnO}_2$  would be formed during oxidation/reduction process at low temperature for shorter contact time to  $\text{H}_2/\text{He}$  gas.

Table 2  
OSC and W/F for  $\text{CuFeO}_2$  and  $\text{CuMnO}_2$ .

Compound	Temperature (°C)	W/F (g s/cm <sup>3</sup> )	OSC (μmol-O <sub>2</sub> /g)
$\text{CuFeO}_2$	350	0.015	211
$\text{CuFeO}_2$	350	0.0075	205
$\text{CuMnO}_2$	300	0.015	68
$\text{CuMnO}_2$	300	0.0075	265

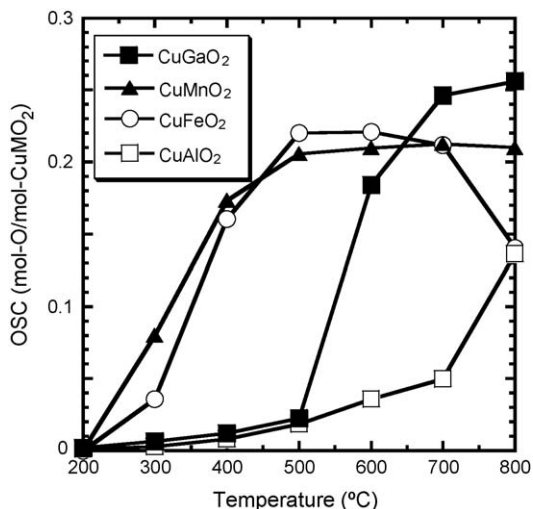


Fig. 8. Amount of oxygen atoms stored in 1 mol of  $\text{CuMO}_2$  as a function of temperature.

Fig. 8 shows the OSC represented by amount of oxygen atoms stored in 1 mol of  $\text{CuMO}_2$ . The oxygen uptake of  $\text{CuFeO}_2$  was 0.16 at 400 °C and increased up to 0.22 at 500 and 600 °C. Formation of non-stoichiometric  $\text{CuFeO}_{2+x}$  was reported by Zhao and co-workers [12] up to  $x = 0.08$  and by Mugnier et al. [7] with  $x$  varying from 0 to 0.18. The oxygen uptake at 400–600 °C exceeded these amounts of extra oxygen,  $x$  and it was found from the XRD results of Fig. 5 that a reductive decomposition occurred at 400–600 °C. These results suggest that the excess oxygen uptake was due to oxidation/reduction cycle between of  $\text{Cu}^+$  and Cu accompanying partial decomposition of  $\text{CuFeO}_{2+x}$ . For other delafossite oxides,  $\text{CuMnO}_2$  and  $\text{CuGaO}_2$ , which decomposed during the OSC measurement, the OSC includes an oxygen uptake attributed to formation of metallic Cu by decomposition of the delafossite phase. In the case of  $\text{CuAlO}_2$ , which remained without decomposition below 800 °C, the oxygen uptake increased with temperature up to 0.13. The OSC value of  $\text{CuAlO}_2$  is smaller than those of  $\text{CuFeO}_2$ ,  $\text{CuMnO}_2$  and  $\text{CuGaO}_2$ , while stability of  $\text{CuAlO}_2$  against oxidation/reduction cycle below 800 °C is higher than that of  $\text{CuFeO}_2$ ,  $\text{CuMnO}_2$  and  $\text{CuGaO}_2$ .

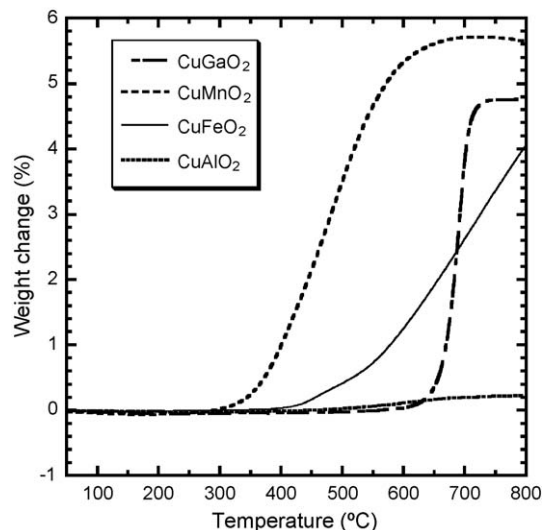


Fig. 9. TG curves of  $\text{CuMO}_2$  measured in air.

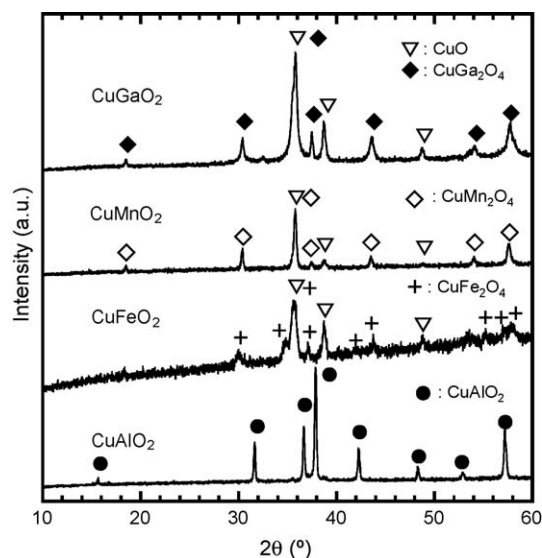
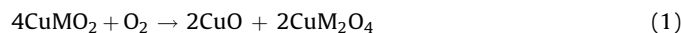


Fig. 10. XRD patterns of  $\text{CuMO}_2$  after TG measurement.



Fig. 9 shows TG curves of  $\text{CuMO}_2$  measured in air. Weight gains were observed for  $\text{CuFeO}_2$ ,  $\text{CuMnO}_2$  and  $\text{CuGaO}_2$ , while little weight change was observed for  $\text{CuAlO}_2$ . The XRD patterns of  $\text{CuMO}_2$  after TG measurements are shown in Fig. 10. In the case of  $\text{CuFeO}_2$ ,  $\text{CuMnO}_2$  and  $\text{CuGaO}_2$ , diffraction peaks are observed for  $\text{CuO}$  and spinel phases such as  $\text{CuFe}_2\text{O}_4$ ,  $\text{CuMn}_2\text{O}_4$  and  $\text{CuGa}_2\text{O}_4$ , respectively. These products contain  $\text{Cu}^{2+}$  instead of  $\text{Cu}^+$  included in delafossite-type oxides. These results indicate that the weight gain observed in the TG curves accompanied oxidation of the delafossite-type oxides according to reaction (1):



Mugnier et al. [7] discussed a tendency for transformation of  $\text{ABO}_2$  delafossite into spinel phase or non-stoichiometric  $\text{ABO}_{2+d}$  (B: trivalent ion) and reported that  $\text{CuB}_2\text{O}_4$  spinel phases are stable for  $\text{B}^{3+}$  ions whose ionic radii are smaller than 0.0665 nm, such as  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{Ga}^{3+}$ . However, in this study, no oxidative decomposition of  $\text{CuAlO}_2$  occurred below 800 °C in air. Further investigation is necessary to confirm the effect of  $\text{M}^{3+}$  using other delafossite-type oxides, such as  $\text{CuM}_{1-x}\text{M}'_x\text{O}_2$  solid solutions.

Reduction behavior of  $\text{CuMO}_2$  was investigated by TPR measurement. TPR curves of  $\text{CuMO}_2$ ,  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  are shown in Fig. 11 and the XRD patterns of  $\text{CuMO}_2$  after the measurements are shown in Fig. 12. Two TPR peaks were observed in the temperature ranges of 300–400 °C and 400–650 °C for  $\text{CuFeO}_2$ . For  $\text{CuMnO}_2$ , two peaks were also observed in the 250–400 °C range.  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  were reduced to  $\text{Cu}$  at 250 and 540 °C, respectively. As reduction of Fe or Mn oxides occurs at higher temperature than reduction of Cu oxide in reductive atmosphere, the reduction peaks observed at lower temperature for  $\text{CuFeO}_2$  and  $\text{CuMnO}_2$  would be attributed to reduction of  $\text{Cu}^+$ , leading to decomposition of the delafossite phases.

The diffraction peaks of Fe and FeO were observed in the XRD pattern for  $\text{CuFeO}_2$ , indicating  $\text{Fe}^{3+}$  in  $\text{CuFeO}_2$  was reduced to  $\text{Fe}^{2+}$  or Fe during the TPR measurement. Therefore, the peak observed at higher temperature would be attributed to reduction of  $\text{Fe}^{3+}$  in  $\text{CuFeO}_2$ . In reductive condition of the OSC measurement using pulse injection,  $\text{Fe}_3\text{O}_4$  formed instead of Fe and FeO, because reaction time between  $\text{CuFeO}_2$  and  $\text{H}_2$  for pulse injection was much shorter than that for the TPR measurement. In the case of  $\text{CuMnO}_2$ , as formation of MnO was observed by the XRD measurement, the

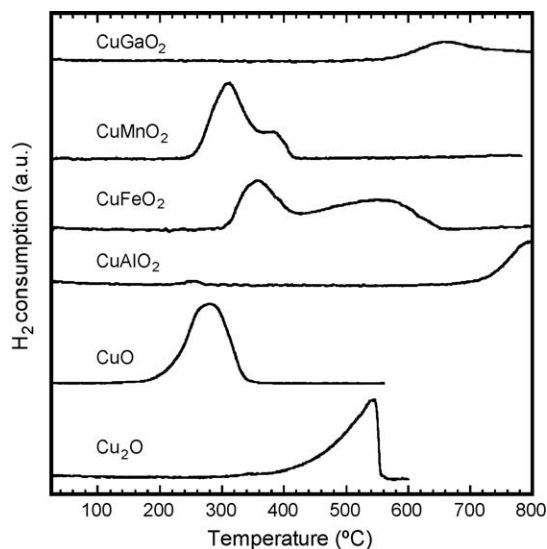


Fig. 11. TPR curves of  $\text{CuMO}_2$  and Cu oxides.

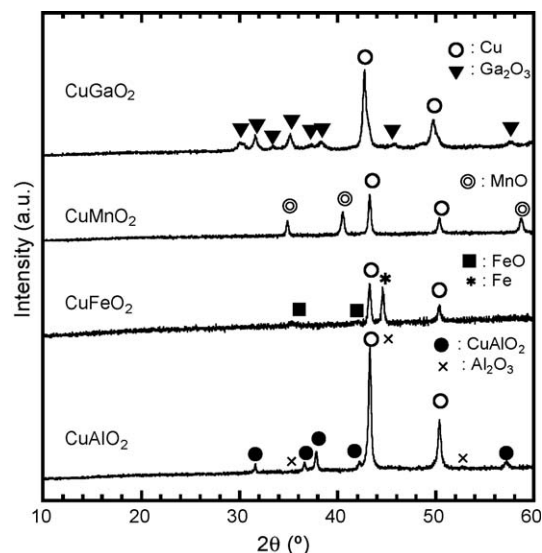
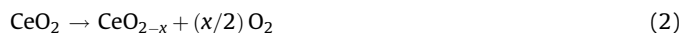


Fig. 12. XRD patterns of  $\text{CuMO}_2$  after TPR measurement.

TPR peak at 350–400 °C would be due to reduction of  $\text{Mn}^{3+}$  to  $\text{Mn}^{2+}$ . For  $\text{CuAlO}_2$  and  $\text{CuGaO}_2$ , reduction occurred above 700 °C and at 550–700 °C, respectively. Particularly, a small amount of the delafossite phase remained for  $\text{CuAlO}_2$ . These results indicate that durability of  $\text{CuAlO}_2$  against reductive atmosphere is higher than that of  $\text{CuFeO}_2$  and  $\text{CuMnO}_2$ , suggesting that reducibility of  $\text{Cu}^+$  in  $\text{CuMO}_2$  can be controlled by M ions at the octahedral sites.

The conventional TWC contains  $\text{CeO}_2$ -based oxide as oxygen storage component.  $\text{CeO}_2$  exhibits oxygen storage/release behavior accompanying the following reactions including the change in oxidation state of Ce.



According to reaction (3), the maximum amount of  $\text{O}_2$  which is released from 1 mol of  $\text{CeO}_2$  is 0.25 mol. However, total OSC value ( $\text{mol-O}_2/\text{mol-Ce}$ ) estimated by TG measurement in 20%  $\text{H}_2$ - $\text{N}_2$  gas is less than 0.1 at 300 °C [13]. And the reversible OSC ( $\text{mol-O}_2/\text{mol-CeO}_2$ ) of  $\text{Pt/CeO}_2/\text{Al}_2\text{O}_3$  catalyst estimated by  $\text{H}_2/\text{O}_2$  pulse injection reported by Kakuta et al. [14] is less than 0.05 at 773–1173 K. The OSC of the delafossite-type  $\text{CuMnO}_2$  was 0.04  $\text{mol-O}_2/\text{mol-CuMO}_2$  (0.08  $\text{mol-O}/\text{mol-CuMO}_2$ ) at 300 °C, which is comparable to that of the  $\text{Pt/CeO}_2/\text{Al}_2\text{O}_3$  catalyst. This suggests that the degrees of reversible oxygen storage/release ability for 1 mol of  $\text{CuMnO}_2$  are comparable to that of  $\text{CeO}_2$  at low temperature, however, these delafossite oxides decomposed under oxidation/reduction cycle above 400 °C.

#### 4. Conclusions

Delafossite-type  $\text{CuMO}_2$  (M = Fe, Mn, Al, Ga) exhibited oxygen storage capacity under oxidation/reduction cycle. OSC values of  $\text{CuFeO}_2$  and  $\text{CuMnO}_2$  at low temperature (<500 °C) are larger than those for  $\text{CuAlO}_2$ ,  $\text{CuGaO}_2$  and  $\text{CeO}_2$ -based materials. The large OSC includes an oxygen uptake at low temperature attributed to formation of metallic Cu by decomposition of the delafossite phase for  $\text{CuFeO}_2$  and  $\text{CuMnO}_2$ . In the case of  $\text{CuAlO}_2$ , which remained without decomposition below 800 °C, the oxygen uptake increased with temperature up to 0.13  $\text{mol-O}/\text{mol-CuMO}_2$ . In order to use the copper containing delafossite-type oxides as an OSC material for a commercial TWC, the further research is necessary to improve the stability at high temperature in oxidative or reductive

atmosphere. In this study, it was found that the oxygen storage behavior of delafossite-type  $\text{CuMO}_2$  compounds can be controlled by a combination of Cu and M ions, therefore,  $\text{CuM}_{1-x}\text{M}'_x\text{O}_2$  solid solutions may be candidate materials which are stable in oxidative and reductive atmospheres at high temperature.

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